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INVESTIGATION OF THE RECOMBINATION PRODUCTS OF ALKYL
RADICALS IN LIQUID-PHASE RADIOLYSIS OF n-HEXANE

By

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INVESTIGATION OF THE RECOMBINATION PRODUCTS OF ALKYL
RADICALS IN LIQUID-PHASE RADIOLYSIS OF n-HEXANE

N. A. Belikova, et al.

Study of the radiolysis of n-hexane is of substantial interest in explaining the features of the radiolysis of liquid n-alkanes. A number of works [1-3] have been devoted to study of the mechanism of radiolysis of n-hexane. However, since the processes occurring during the radiolysis of liquid alkanes are extremely complex, the mechanism of formation of numerous products and their isomer composition have not been explained as yet.

The present work is devoted to a study of the composition of the dimer formed on radiolysis of pure liquid n-hexane and also n-hexane with admixtures of butylene at temperatures of $+20^\circ$ and -77°.

Investigation of the higher products of radiolysis of n-alkanes makes it possible to study the reaction of recombination of alkyl radicals, since the formation of heavy products involves a radical recombination stage. These reactions, at experimental temperatures of $+20^\circ$ and -77°, are practically the only ones in which alkyl radicals can participate; at the moment of formation they are not "hot," and therefore all their reactions, which are secondary from the standpoint

of radiochemistry, occur independently of their origin.

The dimeric product should contain compounds which are a combination of two of the three possible hexyl radicals $CH_3(CH_2)_4\dot{C}H_2$, $CH_3(CH_2)_3\dot{C}HCH_3$ and $CH_3(CH_2)_2CHCH_2CH_3$. All possible recombination products for these radicals are shown in Table 1.

TABLE 1

Probable Isomer Composition of the Dimeric Products of the
Liquid-Phase Gamma-Radiolysis of n-Hexane

Radicals	Radical-recombination products		
R_1 $CH_3(CH_2)_4\dot{C}H_2$	(1,1)*dodecane	(1,2) 5 methyl-undecane	(1,3) 4-ethyl-decane
R_2 $CH_3(CH_2)_3\dot{C}HCH_3$	-	(2,2) 5,6 di-methyldecane	(2,3) 4-ethyl-5-methylnonane
R_3 $CH_3(CH_2)_2CHCH_2CH_3$	-	-	(3,3) 4,5-di ethyloctane

* The figures (1,1), etc., indicate the number of the corresponding recombining radicals [e.g., substance (1,3), or 4-ethyldecane, forms as the result of the recombination of the radicals R_1 and R_3].

In order to obtain standard reference compounds for the identification of the isomer composition of the dimeric product by the method of gas-liquid chromatography, we synthesized all five possible dodecane isomers from recombination of the hexyl radicals (see Table 1).

Experimental

Synthesis of Dodecane Isomers and the Characterization of the Obtained Compounds. The physical properties of the synthesized hydrocarbons, $C_{12}H_{26}$, are given in Table 2.

During the synthesis all unsaturated hydrocarbons $C_{12}H_{26}$ were hydrogenated in the cold over platinum black, while all saturated hydrocarbons were purified by chromatographic adsorption on silica gel.

TABLE 2

Physical Properties of Synthesized Dodecanes

Hydrocarbon	b.p. °C 760 мм	n_D^{20}	d_4^{20}	found MR_D*	found % **	
					C	H
4-ethyldecane	204 — 205	1,4238	0,7550.	57,54	84,81	15,34
					84,60	15,40
5-methylundecane	203 — 204	1,4222	0,7506	57,08	84,58	15,27
					84,55	15,20
4,5-diethyloctane	200 — 201	1,4270	1,7645	57,20	—	—
5,6-dimethyldecane	197 — 198	1,4261	0,7601	57,43	84,70	15,37
					84,41	15,41
4-ethyl-5-methylnonane	194 — 195	1,4269	0,7627	57,33	84,47	15,25
					84,34	15,36

* MR_D calcd. 57.62
** Calcd %: C,84.63; H,15.37.

4-Ethyldecane. The Grignard reaction of 21.5 g Mg, 145 g 1-bromo-hexane, and 73 g ethyl propyl ketone [4] (b.p. 123.2^C (740 mm), n_D^{20} 1.4003) yielded, 4-ethyl-4-decanol in 80% yield, b.p. 127-128° (24 mm), n_D^{20} 1.4424, d_4^{20} 0.8396.

Found %: C 77.02; 76.91; H 14.01; 14.15.

$C_{12}H_{12}O$. Calcd %: C 77.35;   H 14.06.

On distillation of the alcohol at atmospheric pressure in presence of iodine, 4-ethyldecene forms (b.p. 101-105° (24 mm), n_D^{20} 1.4371), and is hydrogenated to 4-ethyldecane.

5-Methylundecane. The Grignard reaction of 23.4 g Mg, 192 g 2-bromooctane (b.p. 66.6-66.8° (9 mm), n_D^{20} 1.4504), and 72 g butyralde-hyde yielded, 88.5 g of reaction products with b.p. 95-130° (10 mm). Distillation of this mixture through a column yielded 33.0 g of 5-methyl-4-undecanol (17% yield), b.p. 118.5-119.0° (10 mm), n_D^{20} 1.4818, d_4^{20} 0.8368. Found: MR_D 58.90; calcd: 59.14.

Found %: C 77.04; 76.74; H 13.84; 13.85.

$C_{12}H_{26}O$. Calcd %: C 77.35;   H 14.06.

5-Methyl-4-undecanol acetate was obtained in 71% yield, b.p.

$117°$ (7 mm), n_D^{20} 1.4302, d_4^{20} 0.8645. Found: MR_D 68.33; calcd: 68.39.

Found %: C 73.54; 7345; H 12.07; 12.18.

$C_{14}H_{28}O_2$. Calcd %: C 73.63; H 12.36.

Pyrolysis of the acetate was conducted at $425°$. The throughput rate was 7-8 ml/hr (tube length 50 cm, diameter 12 mm). The yield of 5-methylundecene was 14.5 g (67%), with b.p. $80-84°$ (12 mm), n_D^{20} 1.4327, n_4^{20} 0.7599. Found: MR_D 57.53; calcd: 57.15.

Found %: C 85.79; 85.88; H 13.78; 14.03.

$C_{12}H_{24}$. Calcd %: C 85.62; H 14.38.

5-Methylundecane was obtained by hydrogenation of 5-methylundecene. The former was distilled through a column with an efficiency of 20 theoretical plates.

4,5-Diethyloctane had been previously obtained by the Würtz reaction from 3-bromohexane [5]; we obtained it in the same manner.

5,6-Dimethyldecane was obtained by the Würtz reaction from 65 g of 2-bromohexane and 10 g of sodium in ether. Yield: 12%.

4-Ethyl-5-methylnonane. The Grignard reaction of 24 g Mg, 165 g 2-bromohexane, and 83.4 g ethyl propyl ketone yielded, 15.2 g 4-ethyl-5-methylnonanol (10% yield), b.p. $126-130°$ (26 mm), n_D^{20} 1.4443. We also obtained a fraction with b.p. $92-97°$ (24 mm), n_D^{20} 1.4280, from which, after chromatographic adsorption on silica gel, 6.5 g of 5,6-dimethyldecane was obtained (7% yield based on 2-bromohexane).

On distillation of 4-ethyl-5-methylnonanol at atmospheric pressure in the presence of iodine we obtained 6.0 g of 4-ethyl-5-methylnonene, b.p. $90-93°$ (22 mm), n_D^{20} 1.4390. By hydrogenation of the latter we obtained 4-ethyl-5-methylnonane.

Conditions of Irradiation and Preparation of Ampules. The method of preparation and irradiation of ampules was similar to that presented

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in a previous work [6]. The amount of pure n-hexane was 8 ml, the total volume of the ampule was ~ 20 ml.

A solution of butylene in n-hexane was prepared by introducing 21 ml of gaseous butylene into the ampule. Irradiation was done with a Co^{60} source at 20° or -77°. The dosage rate was $4.5 \cdot 10^{18}$ ev/ml·hr $\pm$ 10%, the integral dosage was $4.5 \cdot 10^{20}$ ev/ml. The irradiated hexane was transparent in the UV region, while chromatographic analysis data showed only traces of pentane and isomers of hexane as admixtures.

The Method of Chromatographic Analysis. The irradiated samples were analyzed by gas-liquid chromatography at 150°. A chromatographic column was filled with diatomaceous brick saturated with silicone oil PFMS-4 (15 wt.%) as the stationary liquid phase. The column was 500 × 0.6 cm; rate of N_2 feed: 50 ml/min. To increase the sensitivity of the chromatograph, the hydrocarbon was converted to hydrogen. The sensitivity of the instrument was about 6000 mv·ml/mg. The analytical accuracy was, on the average, $\pm$ 7 rel. %. The relative retention times for the isomeric products, $C_{12}H_{26}$, from radiolysis of n-hexane were as follows:

Compound	Relative retention time
Dodecane	1.00*
5-Methylundecane	0.78
4-Ethyldecane	0.78
5,6-Dimethyldecane	0.72
4-Ethyl-5-methylnonane	0.67
4,5-Diethyloctane	0.61

*NB: The retention time of the standard (n-dodecane) was 45 min.

The Experimental Results, and Discussion

The obtained results, averaged for 3-6 measurements, are given in Table 3. The C_9-C_{12} fraction contains, in addition to the above

saturated products, unsaturated hydrocarbons. However, the accumulation of noticeable quantities of these complex products begins with integral dosages one order of magnitude greater [10] than those used in the present work. Even if we consider that on chromatographic analysis of the retention times of these unsaturated hydrocarbons coincide or are very close to the retention times of the observed reference samples of the saturated products, and therefore they come off together, the error introduced by this fact does not exceed $\pm$ 5%. The composition of the products in the C_9-C_{12} fraction was determined, on the average, with an accuracy of $\pm$ 10 rel.%. We should mention that the values of the radiochemical yields were determined only with an accuracy of $\pm$ 20 rel.%, because of the insufficient accuracy of the radiation dosimetry.

TABLE 3

Radiochemical Yields of the Higher Radiolysis Products of n-Hexane

Radiolysis products	Irradiation temperature							
	20°				−77°			
	n-hexane		solution of butylene in n-hexane		n-hexane		solution of butylene in n-hexane	
	number of molecules per 100 ev	%	number of molecules per 100 ev	%	number of molecules per 100 ev	%	number of molecules per 100 ev	%
C_9 isomers	0,11	5,5	0,06	3,4	0,14	10,3	0,04	4,5
n-C_9H_{20}	0,02	1,2	0,02	1,1	0,04	3,0	0,02	1,5
C_{10} isomers	0,12	5,9	0,73	41,0	0,15	11,3	0,38	37,7
n-$C_{10}H_{22}$	0,03	1,3	0,14	8,2	0,04	3,1	0,05	5,6
total C_{10}	0,15	7,2	0,87	49,2	0,19	14,4	0,43	43,3
C_{11} isomers	0,02	1,1	0,02	1,0	0,03	2,0	0,01	0,9
total C_9-H_{11}	0,30	15,0	0,98	54,7	0,39	29,7	0,50	50,2
4,5-diethyloctane	0,30	15,0	0,14	8,5	0,14	10,4	0,06	5,7
4-ethyl-5-methylnonane	0,65	32,6	0,23	12,8	0,26	19,6	0,12	11,5
5,6-dimethyldecane	0,41	20,4	0,19	10,4	0,17	13,3	0,19	9,3
5-methylundecane + 4-ethyldecane	0,31	15,5	0,22	12,5	0,32	23,9	0,20	19,9
n-dodecane	0,03	1,5	0,03	1,7	0,04	3,1	0,03	3,4
total C_{12}	1,70	85,0	0,81	45,3	0,93	70,3	0,50	49,8
total C_9-C_{12}	2,00	100,0	1,79	100,0	1,32	100,0	1,00	100,0

From the experimental data (Table 3) it follows that a drop in the irradiation temperature of n-hexane results in a relative increase in the amount of recombination products of hexyl radicals with fragment

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radicals (and of the fragment radicals with one another) in the C_9-C_{12} fraction. This effect was less pronounced on radiolysis of n-pentane [7].

The primary processes of the reaction of ionizing radiation with the substance should evidently not depend on a change in temperature in the liquid phase from $+20°$ to $-77°$. The reason for a change in the composition of the C_9-C_{12} fraction is associated with a change in the nature or the rate of the secondary chemical reactions or with a change in the properties of the "cage."

In the case of n-hexane radiolysis with butylene admixtures we observe a sharp increase in the absolute and relative content of C_{10} saturated hydrocarbons (to 43-49%) in the C_9-C_{12} fraction. This effect can only be explained by the following secondary chemical reactions:

$$C_4H_8 + H \rightarrow C_4H_9 \qquad (1)$$
$$C_4H_9 + C_6H_{13} \rightarrow C_{10}H_{22} \qquad (2)$$

Let us note that an examination of the final figures in Table 3 shows quite well the inhibiting action of alkanes, familiar from the radiochemical literature, on the radiolysis of compounds with double bonds.

In addition to reaction (1) the reaction $C_4H_8 \leadsto C_4H_7 + H$ is also possible, and then the reaction $C_4H_7 + C_6H_{13} \rightarrow C_{10}H_{20}$ with the formation of a C_{10} compound with a double bond. However, simple calculation shows that with the given ratio of the butylene and hexane concentrations, even if we consider the slight difference in the radiochemical yields and the inhibiting effect of butylene on radiolysis of hexane, this reaction constitutes no more than 1-2% of reaction (1).

Thus we can consider it established that on radiolysis of alkanes in the liquid phase the thermal hydrogen atoms add to the unsaturated

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products; as a result of this reaction an aliphatic radical forms. The ease with which H atoms and radicals add to the multiple bonds has been noted frequently in the literature; in particular, there has been mentioned [8] the assumption that this fact can be explained by the relatively low energy required to break the π-bond.

Therefore, on radiolysis of liquid n-hexane (in absence of butylene) it is necessary, when examining the possible ways for the formation of the dimer, in addition to the reactions

$$C_6H_{14} \rightsquigarrow \dot{C}_6H_{13} + H \tag{3}$$
$$C_6H_{14} + H \rightarrow C_6H_{13} + H_2 \tag{4}$$

to also take into account the reaction

$$C_6H_{12} + \dot{H} \rightarrow \dot{C}_6H_{13} \tag{5}$$

since hexene is one of the products of radiolysis of n-hexane. In our experiments the concentration of butylene in hexane was $13 \cdot 10^{-2}$ mole/l, while the calculated concentration of hexenes (at $G = 1.8$ molecules/100 ev [2]) at the end of the experiment did not exceed $1.3 \cdot 10^{-2}$ mole/l, i.e., about 0.1 of the concentration of the butylenes. Consequently, on radiolysis of n-hexane with butylene admixtures reaction (1) predominates over reaction (5).

Certain conclusions on the relative steady-state concentration of the hexyl radicals formed on irradiation can be drawn on the basis of knowledge of the isomer composition of the dimer product, since the only way in which it can be obtained is by recombination of the hexyl radicals (the yields of a reaction of the type $R_i + R_j \rightarrow C_{12}$ are negligibly small due to the insignificant steady-state concentrations of these radicals). As follows from the data in Table 3, all possible isomers of the dimeric product form on n-hexane radiolysis.

Assuming [7] that the rate of formation of the dimer products in

the liquid phase is proportional to the steady-state concentration of the corresponding radicals, and allowing that the recombination constants of the hexyl radicals with a straight carbon chain are practically identical, we can compile a system of six equations for the formation of five branched dodecanes and of n-dodecane (see Table 1 for the designations):

$$\frac{dC_{1,1}}{dt} = \frac{1}{2} k R_1^2 \qquad (6)$$

$$\frac{dC_{2,2}}{dt} = \frac{1}{2} k R_2^2 \qquad (9)$$

$$\frac{dC_{1,2}}{dt} = k R_1 R_2 \qquad (7)$$

$$\frac{dC_{2,3}}{dt} = k R_2 R_3 \qquad (10)$$

$$\frac{dC_{1,3}}{dt} = k R_1 R_3 \qquad (8)$$

$$\frac{dC_{3,3}}{dt} = \frac{1}{2} k R_3^2 \qquad (11)$$

After simple transformations we get

$$R_2/R_1 = \sqrt{\rho_{2,2}/\rho_{1,1}} \qquad (12)$$

$$R_2/R_3 = \frac{1}{2} \frac{\rho_{2,3}}{\rho_{3,3}} \qquad (15)$$

$$R_3/R_1 = \sqrt{\rho_{3,3}/\rho_{1,1}} \qquad (13)$$

$$\frac{R_2 + R_3}{R_1} = \frac{1}{2} \frac{\rho_{1,2} + \rho_{1,3}}{\rho_{1,1}} \qquad (16)$$

$$R_2 R_3 = \frac{1}{2} \rho_{2,3} \rho_{3,3} \qquad (14)$$

$$\frac{R_2 + R_3}{R_1} = \sqrt{\frac{\rho_{2,2}}{\rho_{1,1}}} + \sqrt{\frac{\rho_{3,3}}{\rho_{1,1}}} \qquad (17)$$

where ρ is the percent content of the isomers, determined from gas-liquid chromatography data.

The values of the relative concentrations of the radicals calculated from Eqs. (12)-(17) are given in Table 4. The ratios R_2/R_3 and $(R_2 + R_3)/R_1$, calculated from various equations, quite satisfactorily agree. Consequently, the constant of the rate of recombination of hexyl radicals with the straight carbon chain in the liquid phase is actually not a function, for all practical purposes, of their nature. This example illustrates the possibility of using radiochemical methods to investigate the mechanism and the kinetics of radical reactions in the liquid phase. In particular, by studying the radiolysis of isomeric hexanes we can obtain interesting data on the behavior of isomeric hexyl radicals in solution.

TABLE 4

Ratio of Concentrations of Hexyl Radicals Formed on Liquid-Phase
Gamma-Radiolysis of n-Hexane

Ratio	Calculated according to equation	Irradiation temperature	
		20°	-77°
R_2/R_1	(12)	3.7	2.1
R_3/R_1	(13)	3.2	1.9
R_2/R_3	(14)	1.2	1.1
R_2/R_3	(15)	1.1	0.9
$(R_2 + R_3)/R_1$	(16)	5.2	3.9
$(R_2 + R_3)/R_1$	(17)	6.9	4.0

As can be seen from the data in Table 4, the concentration of each of the radicals R_2 and R_3 at $+20^\circ$ is $\sim$ 3.5-times greater than that of the primary radical, while the concentrations of the R_2 and R_3 radicals are approximately identical. At a temperature of -77° we have $R_2/R_1 \sim R_3/R_1 \sim 2$ and also $R_2 \cong R_3$.

These ratios cannot be associated with the hypothesis to the effect that because of the high electron energy (in steady-state distribution of the order of several tens of ev) the probability of the abstraction of a H atom in a certain position is determined only by how frequently they are encountered in a given molecule; actually, on this basis there should have been the following ratio: $R_1:R_2 = 6:4$.

Our results agree qualitatively with the familiar results of Rice and other authors, according to which R_2/R_1 and R_3/R_1 are of the order of several units and $R_2 \cong R_3$ for the thermochemical reactions of alkanes in the gas phase. Such a coincidence, naturally, cannot be fortuitous.

Rice and other authors have explained this fact by the influence of the difference in abstraction energy of the secondary and primary

H atoms (this difference is ~ 0.25 ev); such an explanation can hardly be directly applicable to our case, since one of the possible ways for the formation of radicals is the hydrogenation of hexenes.

Actually, in order that such an energy difference, which is insignificant compared with the average energy of the steady-state distribution of electrons, can influence the probability of the abstraction of various bonds, one of the following must be assumed: 1) abstraction of a certain H atom from the hexane occurs not at the "site" of electron impact, but after the considerable energy obtained by the molecule during this impact has some way been distributed throughout all or most of the molecule bonds; only after such redistribution can the ~ 0.25 ev be essential for the probability of the abstraction of an H atom, as can be easily seen from the elementary chemical kinetics; 2) the molecule can with maximum probability obtain, on collision with an electron, or transmit to some bond, the energy of the order of the energy of the bonds.

Table 5 gives the percentage composition of the products of recombination of hexyl radicals. As can be seen from an examination of this table, n-dodecane $(R_1 + R_1)$ forms in a quantity which is 10-times less than the products $R_1 + R_2$ and $R_1 + R_3$ at 20° and 8-times less at -77°, while the calculated concentration of the hexyl radical R_1 is 3.5 and 2-times less than the concentration of each of the R_2 and R_3 radicals, respectively.

The role of n-dodecane in the dimerization products of hexyl radicals is therefore negligible, and is 1.8% and 4.3% at $+20^{\circ}$ and -77° respectively. At 20°, 80% of the dimer product, and at -77° about 61%, is obtained due to the reaction of the secondary radicals $(R_2 + R_2, R_2 + R_3, R_3 + R_3)$.

TABLE 5

Radiochemical Yields of Recombination Products on Hexyl Radicals on Liquid-Phase Gamma-Radiolysis of n-Hexane

Recombining radicals	Yield			
	Exptl Temp. +20°		Exptl Temp. -77°	
	molecules per 100 ev	%	molecules per 100 ev	%
$R_3 + R_3$	0.30	17.6	0.14	15.1
$R_2 + R_3$	0.65	38.3	0.26	28.0
$R_2 + R_2$	0.41	24.1	0.17	18.2
$R_1 + R_2$				
$R_1 + R_3$	0.31	18.2	0.32	34.4
$R_1 + R_1$	0.03	1.8	0.04	4.3

With a change in the radiolysis temperature of n-hexane from +20° to -77° the yield of the various C_{12} isomers changes in various ways: the yield of the isomers formed with the participation of secondary radicals (4,5-diethyloctane, 4-ethyl-5-methylnonane, and 5,6-dimethyl-decane) decreases by a factor of 2.2-2.4, while the yield of the "primary" products (5-methylundecane, 4-ethyldecane, and n-dodecane) remains practically constant. These ratios are also preserved on radiolysis of n-hexane with added butylene.

Since 1) the recombination rate constant for all hexyl radicals is identical, and 2) the rate of generation of various radicals by electron impact is practically independent of temperature (in any event, in the temperature range in our experiments), the total decrease (approximately two-fold) of the yield of the dimer product can be explained only by the increased probability of reverse recombination of a H atom and the hexyl radical directly or immediately after they form, or by a change in the hydrogenation reaction rate.

On the basis of the obtained experimental data we can evaluate the steady-state concentration of thermal hydrogen atoms. For this we must use data on the radiochemical yields of $C_{10}H_{22}$ in experiments on hexane radiolysis with butylene additives.

On irradiation, in hexane there occurs steady-state concentration of the C_4H_9, i.e., the rate of its formation equals the rate of its disappearance:

$$\frac{d[C_4H_9]}{dt} = k_1[H][C_4H_x] = -\frac{d[C_4H_9]}{dt} = k_2[C_4H_9][C_6H_{13}]. \tag{18}$$

Expression (18) will be accurate, e.g., for cyclohexane; only the cyclohexyl radical will form, for all intents and purposes, on radiolysis of cyclohexane. For the case of hexane and other alkanes, we must also take into account the reactions with the fragment radicals of breaking the bonds C - C, i.e., a term of the type $k_4[C_4H_9] \cdot [\sum_i R_i]$, where i in the case of hexane changes from 1 to 5. Since the fragment radicals are ~ 30% of the alkyl radicals, disregard of this term indicates that the calculation is significant only in order of magnitude.

Consequently,

$$\frac{d[C_{10}H_{22}]}{dt} = k_2[C_4H_9][C_6H_{13}] = k_1[H][C_4H_x]. \tag{19}$$

$$w = \frac{d[C_{10}H_{22}]}{dt} = \frac{GM}{10^2 \cdot 6{,}0_2 \cdot 10^{23}} \text{ mole/sec} \cdot 1 \tag{20}$$

where $\underline{w}$ is the rate of formation of $C_{10}H_{22}$ in mole/sec·l; G is the radiochemical yield of $C_{10}H_{22}$ in mole/100 ev; M is the power of the dosage in ev/l·sec.

The steady-state concentration of thermal hydrogen atoms is defined by the formula

$$[H] = \frac{w}{k_1[C_4H_x]} \cdot \tag{21}$$

The steady-state concentration ($k_1 = 6 \cdot 10^8$ l/mole·sec) for a reaction in the gaseous phase [9]:

$$[H] = \frac{1.8 \cdot 10^{-8} \text{ mole/l} \cdot \text{sec}}{6 \cdot 10^{8} \text{ l/mole} \cdot \text{sec} \; 0.13 \text{ mole/l}} \approx 2.3 \cdot 10^{-16} \text{ mole/l}.$$

The steady-state concentration of radicals in our case, according to Wagner [7], can be defined by the equation

$$[R] = (k_g J/k_p)^{1/2} = \left(\frac{1.43 \cdot 10^{-11} \cdot 0.3 \cdot 10^{6}}{1 \cdot 10^{10}}\right)^{1/2} = 0.6 \cdot 10^{-8} \text{ mole/l},$$

where $k_p = 1 \cdot 10^{10}$ 1/mole·sec is the constant of the rate of recombination of the radicals in the gas.

Thus, $[R]/[H] \approx 2.6 \cdot 10^{7}$.

Naturally, the steady-state concentration of H atoms will be higher in the absence of butylene admixtures, due to the inhibiting effect of these latter on radiolysis. However, this inhibition does not exceed ~ 25-30% (see Table 3), so that there is also no evaluation regarding order of magnitude for the case of radiolysis without butylene admixtures.

The calculation has shown that the recombination of thermal hydrogen atoms with one another and with alkyl radicals, for the given dosage power, cannot be reckoned from the moment the hexane concentration exceeds ~ 10^{-7} mole/l, i.e., even with very small integral dosages. In the calculation we have assumed that either k_g and k_p have the same value for the gaseous and liquid phase, or they change by the same factor on transition from a gas to a liquid.

Conclusions

1. We have studied experimentally the fraction C_9-C_{12} of the higher products of the liquid-phase gamma-radiolysis of pure n-hexane and n-hexane with added butylene at $+20^{\circ}$ and -77°.

2. We have investigated in detail the isomer composition of the dimer product of the radiolysis of n-hexane, and explained certain properties of the various hexyl radicals.

3. We have calculated the relative steady-state concentrations of hexyl radicals and shown that the constants of the recombination of various hexyl radicals with a straight carbon chain are practically equal in the liquid phase.

5. We have synthesized for the first time four isomers of dodecane and determined their physical properties.

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